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# Efficient $\text{Ni}^{\text{II}}\text{Ln}^{\text{III}}_2$ Electrocyclization Catalysts for the Synthesis of *trans*-4,5-Diaminocyclopent-2-enones from 2-Furaldehyde and Primary or Secondary Amines

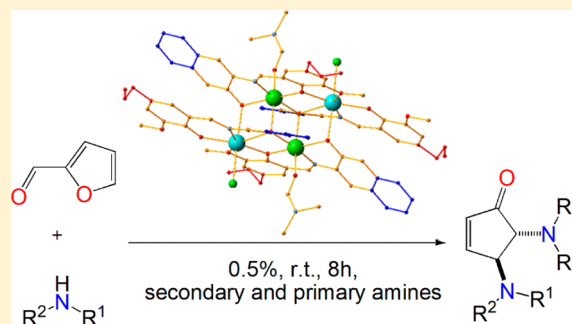
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## Supporting Information

**ABSTRACT:** A series of heterometallic coordination clusters (CCs) [ $\text{Ni}^{\text{II}}\text{Ln}^{\text{III}}_2(\text{L1})_4\text{Cl}_2(\text{CH}_3\text{CN})_2$ ]  $2\text{CH}_3\text{CN}$  [ $\text{Ln} = \text{Y}$  (**1Y**),  $\text{Sm}$  (**1Sm**),  $\text{Eu}$  (**1Eu**),  $\text{Gd}$  (**1Gd**), or  $\text{Tb}$  (**1Tb**)] were synthesized by the reaction of (E)-2-(2-hydroxy-3-methoxybenzylidene-amino)phenol ( $\text{H}_2\text{L1}$ ) with  $\text{NiCl}_2 \cdot 6(\text{H}_2\text{O})$  and  $\text{LnCl}_3 \cdot x(\text{H}_2\text{O})$  in the presence of  $\text{Et}_3\text{N}$  at room temperature. These air-stable CCs can be obtained in very high yields from commercially available materials and are efficient catalysts for the room-temperature domino ring-opening electrocyclization synthesis of *trans*-4,5-diaminocyclopent-2-enones from 2-furaldehyde and primary or secondary amines under a non-inert atmosphere. Structural modification of the catalyst to achieve immobilization or photosensitivity is possible without deterioration in catalytic activity.

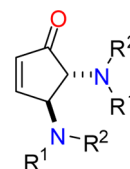


## INTRODUCTION

Polynuclear coordination clusters (CCs),<sup>1,2</sup> assembled from organic ligands, transition-metal elements (3d), and/or lanthanide (4f) elements, are a burgeoning class of functional materials with fascinating structures.<sup>3–8</sup> These materials are already used in areas ranging from molecular magnetism,<sup>9–17</sup> biology,<sup>18–20</sup> molecular imaging,<sup>21</sup> magnetic resonance,<sup>22</sup> and luminescence.<sup>23–27</sup> However, one of the most common applications for coordination compounds, catalysis, is much less studied for polynuclear 3d/4f heterometallic CCs with classical N,O-donor ligands<sup>28–34</sup> than for organometallic compounds.<sup>35,36</sup> The difference in the growth rates between the two research fields may reflect the fact that organometallic compounds are mainly of low nuclearity, so it is easier to determine a possible mechanism for the catalytic procedure.

Electrocyclizations are one of the most valuable transformations for the construction of carbon–carbon bonds. The Nazarov cyclization exemplifies such an electrocyclization, providing access to important and useful cyclopentenones, and Lewis acids catalyze this cyclization.<sup>37–39</sup> The interest in bifunctionalized cyclopentenones arises from the fact that they are versatile building blocks in the synthesis of natural products such as (+)-Nakadomarin A.<sup>40</sup> Batey and Li used a variety of Lewis acids for the synthesis of *trans*-4,5-diaminocyclopentanones (Scheme 1) from the domino condensation/ring-opening/electrocyclization reaction of furfuraldehyde with amines.<sup>41</sup> In this study,  $\text{Dy}(\text{OTf})_3$  and  $\text{Sc}(\text{OTf})_3$  were found to be the best catalysts, with 10% loadings. However,  $\text{Sc}(\text{OTf})_3$

**Scheme 1. Schematic Representation of *trans*-4,5-Diaminocyclopentanones**



gave higher yields with primary anilines ( $\text{R}^2 = \text{H}$ ; see Scheme 1) than  $\text{Dy}(\text{OTf})_3$ . This reaction proceeds in high yields with the use of acidic ionic liquids under solvent-free conditions<sup>42</sup> or with the use of *N*-sulfonylimine, with *p*-toluenesulfonamide acting as a leaving group.<sup>43</sup> However, in both cases, the reaction works only for secondary amines.

We have recently developed a new generation of 3d/4f CCs and have explored their catalytic behavior. The Schiff base  $\text{H}_2\text{L1}$  (Scheme S1 in the Supporting Information), along with 3d and 4f ions affords tetranuclear  $\text{M}^{\text{II}}_2\text{Ln}^{\text{III}}_2$  ( $\text{M} = \text{Co}$  or  $\text{Ni}$ ) CCs possessing a defect dicubane topology with two divalent 3d ions (center) and two trivalent 4f ions (wings) (Scheme S1, middle).<sup>45,46</sup> In this specific topology, five out of six, and six out of seven or eight, coordination sites are occupied by  $\text{H}_2\text{L1}$  for the 3d and the  $\text{Dy}^{\text{III}}$  centers, respectively (Scheme S1, right). Recently, we reported that compound  $[\text{Ni}^{\text{II}}_2\text{Dy}^{\text{III}}_2(\text{L1})_4]$

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$\text{Cl}_2(\text{CH}_3\text{CN})_2] \cdot 2\text{CH}_3\text{CN}$  (**1Dy**) exhibits similar catalytic efficiency, with only 1% loading. This CC, unlike  $\text{Dy}(\text{OTf})_3$ , could catalyze the reaction with secondary and primary amines.<sup>41,47</sup> In our quest to develop these catalytic species further and to (a) seek lower cost materials and (b) investigate its possibility of immobilization, we decided to (i) extend our study to other lanthanides and (ii) to tune the organic periphery of the  $\text{H}_2\text{L1}$  ligand. Synthetic, catalytic, and theoretical issues are discussed in this report.

## EXPERIMENTAL SECTION

**Materials and methods.** *Materials.* Chemicals (reagent grade) were purchased from Sigma–Aldrich and Alfa Aesar. All experiments were performed under aerobic conditions, using materials and solvents as received.

*Instrumentation.* NMR spectra were recorded on a Varian VNMRs solution-state spectrometer at 500 MHz at 30 °C using residual isotopic solvent ( $\text{DMSO}$ ,  $\delta_{\text{H}} = 2.50$  ppm) as an internal reference. Chemical shifts are quoted in parts per million (ppm). Coupling constants ( $J$ ) are recorded in units of Hz. IR spectra of the samples were recorded over the range of 4000–650  $\text{cm}^{-1}$  on a PerkinElmer Spectrum One FT-IR spectrometer fitted with an UATR polarization accessory. ESI-MS data were obtained on a VG Autospec Fissions instrument (EI at 70 eV). TGA analysis was performed on a TA Instruments Q-50 model (TA, Surrey, U.K.) under nitrogen and at a scan rate of 10 °C/min.

*Synthetic Procedures.* For the synthesis of ligands, see the Supporting Information (ESI).

**Synthesis of 1Ln (Ln = Y, Sm, Eu, Gd, Tb, Dy).**  $\text{H}_2\text{L1}$  (0.2 mmol, 48 mg), and  $\text{Et}_3\text{N}$  (0.5 mmol, 69  $\mu\text{L}$ ) were added to a solution of MeCN (20 mL), and that mixture was stirred for 10 min.  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.1 mmol, 24 mg) and  $\text{LnCl}_3 \cdot x\text{H}_2\text{O}$  (0.1 mmol) (Ln = Y, Nd, Sm, Eu, Gd, Tb, Dy) were added, and the resultant solution was heated under reflux for 2 h. During this time, a green precipitate was formed from the yellow solution. The precipitant was filtered off and then washed with cold MeCN (20 mL) and  $\text{Et}_2\text{O}$  (10 mL). The precipitate (**1Ln**) was then collected and dried overnight at 60 °C. Yield = 69%–95%, based on Ln (for **1Ln**). Elemental analysis for  $\text{Ni}_2\text{Dy}_2(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4\text{Cl}_2(\text{CH}_3\text{CN})_2$  (**1Dy**): C 46.55, H 3.23, N 5.38; found C 46.84, H 3.21, N 5.16. Elemental analysis for  $\text{Ni}_2\text{Y}_2(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4\text{Cl}_2(\text{CH}_3\text{CN})_2$  (**1Y**): C 51.06, H 3.57, N 5.95; found C 51.32, H 3.51, N 6.09. Elemental analysis for  $\text{Ni}_2\text{Gd}_2(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4\text{Cl}_2(\text{CH}_3\text{CN})_2$  (**1Gd**): C 46.15, H 3.25, N 5.42; found C 46.51, H 3.18, N 4.82. Elemental analysis for  $\text{Ni}_2\text{Eu}_2(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4\text{Cl}_2(\text{CH}_3\text{CN})_2$  (**1Eu**): C 46.81, H 3.47, N 5.46; found C 47.08, H 3.79, N 5.52. Elemental analysis for  $\text{Ni}_2\text{Tb}_2(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4\text{Cl}_2(\text{CH}_3\text{CN})_2$  (**1Tb**): C 46.85, H 3.25, N 5.42; found C 47.20, H 3.33, N 4.98. Elemental analysis for  $\text{Ni}_2\text{Sm}_2(\text{C}_{14}\text{H}_{11}\text{NO}_3)_4\text{Cl}_2(\text{CH}_3\text{CN})_2$  (**1Sm**): C 46.87, H 3.28, N 5.16; found: C 46.81, H 3.22, N 4.91.

**Synthesis of Compounds 2Y, 3Y, and 4Y.** *Compound 2Y.* To a solution of MeCN (20 mL),  $\text{H}_2\text{L2}$  (0.2 mmol), and  $\text{Et}_3\text{N}$  (0.5 mmol, 69  $\mu\text{L}$ ) were added and the mixture was stirred for 10 min.  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.1 mmol, 24 mg) and  $\text{YCl}_3 \cdot x\text{H}_2\text{O}$  (0.1 mmol, 30 mg) were added and the resultant solution was heated under reflux for 2 h. The brown precipitate that settled as the mixture was allowed to cool was filtered and washed off with cold MeCN (20 mL) and  $\text{Et}_2\text{O}$  (10 mL). The precipitate was then collected and dried overnight at 60 °C. Yield: 65%, based on Y. Crystals for single-crystal X-ray diffraction (XRD) were obtained by dissolving **2Y** (25 mg) in DMF (10 mL). The solution was stirred for 10 min before filtration. The filtrate underwent vapor diffusion with  $\text{Et}_2\text{O}$ ; after 7 days, large brown crystals suitable for XRD study were obtained. Elemental analysis for  $\text{Ni}_2\text{Y}_2(\text{C}_{17}\text{H}_{15}\text{NO}_3)_4\text{Cl}_2(\text{CH}_3\text{CN})_2$  (**2Y**): C 55.02, H 4.23, N 5.35; found: C 55.04, H 4.64, N 5.16.

*Compound 3Y.* To a solution of MeCN (20 mL),  $\text{H}_2\text{L3}$  (0.2 mmol), and  $\text{Et}_3\text{N}$  (0.5 mmol, 69  $\mu\text{L}$ ) were added and the mixture was stirred for 10 min.  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.1 mmol, 24 mg) and  $\text{YCl}_3 \cdot x\text{H}_2\text{O}$

(0.1 mmol, 30 mg) were added and the resultant solution was heated under reflux for 2 h. The brown/yellow precipitate that settled as the mixture was allowed to cool was filtered and washed off with cold MeCN (20 mL) and  $\text{Et}_2\text{O}$  (10 mL). The precipitate was then collected and dried overnight at 60 °C. Yield = 74%, based on Y. Crystals for single-crystal XRD were obtained by dissolving **3Y** (25 mg) in DMF (10 mL). The solution was stirred for 10 min before filtration. The filtrate underwent vapor diffusion with  $\text{Et}_2\text{O}$ ; after 12 days clear green crystals suitable for XRD study were obtained. Elemental analysis for  $\text{Ni}_2\text{Y}_2(\text{C}_{18}\text{H}_{13}\text{NO}_3)_4\text{Cl}_2(\text{CH}_3\text{CN})_2$  (**3Y**): C 56.31, H 3.97, N 5.02; found: C 56.64, H 3.63, N 5.21.

*Compound 4Y.* To a solution of MeCN (20 mL),  $\text{H}_2\text{L4}$  (0.2 mmol), and  $\text{Et}_3\text{N}$  (0.5 mmol, 69  $\mu\text{L}$ ) were added and the mixture was stirred for 10 min.  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.1 mmol, 24 mg) and  $\text{YCl}_3 \cdot x\text{H}_2\text{O}$  (0.1 mmol, 30 mg) were added and the resultant solution was heated under reflux for 2 h. The brown/red precipitate that settled as the mixture was allowed to cool was filtered and washed off with cold MeCN (20 mL) and  $\text{Et}_2\text{O}$  (10 mL). The precipitate was then collected and dried overnight at 60 °C. Yield: 90%, based on Y. Crystals for single-crystal XRD were obtained by dissolving **4Y** (25 mg) in DMF (10 mL). The solution was stirred for 10 min before filtration. The filtrate underwent vapor diffusion with  $\text{Et}_2\text{O}$ ; after 3 weeks, small green crystals suitable for XRD study were obtained. Elemental analysis for  $\text{Ni}_2\text{Y}_2(\text{C}_{21}\text{H}_{17}\text{NO}_3)_4\text{Cl}_2(\text{CH}_3\text{CN})_2$  (**4Y**): C 59.65, H 4.21, N 4.74; found: C 59.84, H 3.60, N 4.92.

**General Catalytic Protocol.** In air, powdered 4 Å molecular sieves (100 mg) were weighed into a 10 mL capped vials equipped with magnetic stirring bars. The use of molecular sieves is crucial for the reaction, since 1 equiv of water is generated as a side product. MeCN (dry, 4 mL), furfural (0.5 mmol, 41  $\mu\text{L}$ ), secondary amine (1 mmol), and the appropriate amount of catalyst (10%–1% total Dy) were added. The mixture was stirred at room temperature from 2 to 24 h, and the reaction was followed by thin layer chromatography (TLC). The reaction mixture was diluted with DCM (20 mL) and filtered through Celite. The resultant solution was concentrated under reduced pressure and the residue purified by column chromatography (20%–30% ethyl acetate in hexanes). The products were obtained as red or yellow oils, which solidified on standing.

**Crystallography.** Data for **2Y**, **3Y**, and **4Y** ( $\omega$ -scans) were obtained at the University of Sussex by use of an Agilent Xcalibur Eos Gemini Ultra diffractometer with CCD plate detector under a flow of nitrogen gas at 173(2) K using Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). CRYSLIS CCD and RED software programs were used, respectively, for data collection and processing. Reflection intensities were corrected for absorption by the multiscan method. Data for **1Sm-A**, **1Sm-B**, **1Sm-C**, and **1Eu-A** were collected at the UK National Crystallography Service, University of Southampton<sup>48</sup> on a Rigaku Saturn 724+ area detector mounted at the window of an FR-E+ rotating anode generator with a Mo anode ( $\lambda = 0.71075$  Å) under a flow of nitrogen gas at 100(2) K. The X-ray data were collected and processed using Rigaku CrystalClear, except **1Eu-A**, where Rigaku Oxford Diffraction CrystallisPro was used for data processing. Crystal structures **1Sm-B**, **2Y**, and **4Y** were solved by dual-space methods with SHELXT,<sup>49</sup> whereas **1Sm-A**, **1Sm-C**, **1Eu-A**, and **3Y** were solved using charge flipping methods with Superflip.<sup>50</sup> All crystal structures were then refined on  $F_o^2$  by full-matrix least-squares refinements using SHELXL.<sup>49</sup> All non-H atoms were refined with anisotropic thermal parameters, and H atoms were introduced at calculated positions and allowed to ride on their carrier atoms. Geometric/crystallographic calculations were performed using PLATON,<sup>51</sup> Olex2,<sup>52</sup> and WINGX<sup>53</sup> packages; graphics were prepared with Crystal Maker.<sup>54</sup> Crystallographic details are given in Table S1 in the ESI (CCDC Nos. 1442674–1442680).

**Computational Details.** Energy minimization calculations on strategically designed model compounds (see Results and Discussion) were made within the Kohn–Sham density functional theory (DFT) approach at the B3LYP/SDD and B3LYP/6-311G\* levels,<sup>55–65</sup> with the Gaussian 09<sup>66</sup> software. The Jmol program was used for visualization purposes.<sup>67</sup>



## RESULTS AND DISCUSSION

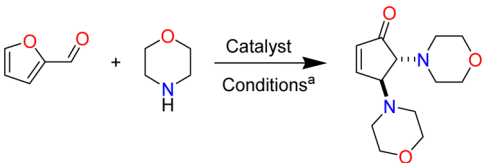
With the goal of developing effective molecular catalysts with low cost, we reasoned that replacement of Dy<sup>III</sup> with lanthanides of lower cost would allow us to evaluate the relationship between cost and effectiveness. Thus, we attempted to isolate and characterize the analogues of compound **1Dy** with Y (**1Y**), Sm (**1Sm**), Eu (**1Eu**), Gd (**1Gd**), and Tb (**1Tb**), following the similar reaction procedure that gave **1Dy**.<sup>47</sup> The synthetic protocol specifies that, when the blend Dy(OTf)<sub>3</sub>/Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O or NiCl<sub>2</sub>·6H<sub>2</sub>O/H<sub>2</sub>L1/Et<sub>3</sub>N (molecular ratio of 1/1/2/5) in CH<sub>3</sub>CN (20 mL) is refluxed for 1 h, the result, after filtration, is the formation of yellow-greenish crystals in moderate yield. Since the reactions to produce the **1Y**, **1Sm**, **1Eu**, **1Gd**, and **1Tb** gave large amounts of filtrate, we decided to further characterize the constituent species. A range of techniques such as ESI-MS, elemental analysis, infrared (IR) spectroscopy, and TGA showed that these filtrates were similar to that from **1Dy**. IR spectra of **1Y**, **1Sm**, **1Eu**, **1Gd**, and **1Tb** are similar to that of **1Dy** (see the ESI). The TGA data (Figures S12–S17 in the ESI) for all solid compounds indicated the loss of four CH<sub>3</sub>CN molecules (lattice and coordinated) up to 290 °C and decomposition at higher temperatures. ESI-MS spectra of all species were similar, with two main peaks corresponding to the {[Ni<sup>II</sup><sub>2</sub>Ln<sup>III</sup><sub>2</sub>(L1)<sub>4</sub>Cl(CH<sub>3</sub>CN)(CH<sub>3</sub>OH)]+4H}<sup>+</sup> and -{[Ni<sup>II</sup><sub>2</sub>Ln<sup>III</sup><sub>2</sub>(L1)<sub>4</sub>]}<sup>2+</sup> fragments (Figures S1–S7 in the ESI). Finally, elemental analyses are consistent with the calculated values without lattice CH<sub>3</sub>CN molecules. IR, TGA, and ESI-MS analyses were performed three times from different batches, with similar results.

In our attempts to grow crystals, several unexpected products were structurally characterized, indicating that the synthesis of these species is not a simple task.<sup>68</sup> For example, our effort to obtain crystals of **1Sm** resulted in the structural characterization of three different compounds, formulated as [Ni<sup>II</sup><sub>2</sub>Sm<sup>III</sup><sub>2</sub>(CO<sub>3</sub>)-(L1)<sub>7</sub>(L')(H<sub>2</sub>O)<sub>3</sub>] (**1Sm-A**), [Ni<sup>II</sup><sub>2</sub>Sm<sup>III</sup><sub>2</sub>(L1)<sub>4</sub>(O-Van)<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub>]·4CH<sub>3</sub>CN (**1Sm-B**), and [Sm<sup>III</sup><sub>4</sub>(OH)<sub>2</sub>(L1)<sub>4</sub>(HL1)<sub>2</sub>]·2CH<sub>3</sub>CN (**1Sm-C**), where L' is 2-aminophenol and O-Van is *ortho*-vanillin (see the ESI). In our attempt to obtain crystals of **1Eu**, a compound formulated as [Ni<sup>II</sup><sub>2</sub>Eu<sup>III</sup><sub>4</sub>(L1)<sub>8</sub>(CO<sub>3</sub>)<sub>4</sub>Cl·(H<sub>2</sub>O)<sub>14</sub>] (**1Eu-A**) was obtained. The latter molecule is isoskeletal to compounds recently reported by Ke et al.<sup>69</sup>

The next step was to characterize the catalytic activity of these species using the catalytic protocol developed in our previous study.<sup>47</sup> In order to ascertain that the catalytic activity of these species is driven solely by the 4f ions, various blank tests were performed (see Table S1). First, three Ni<sup>II</sup> salts with three different loadings (Table S1, entries 2–10) were used in the prototype reaction. NiCl<sub>2</sub> was found to catalyze the reaction with very high loadings and very low yields after 24 h (Table S2 in the ESI, entry 2) reflecting that its contribution is negligible for the shorter time period. An *in situ* mixture of Ni salt and ligand (Table S2, entries 11–13) gave none of the anticipated product after 24 h. In Batey's protocol,<sup>41</sup> since Dy(OTf)<sub>3</sub> was found to be an excellent catalyst using a loading of 10 mol %, our next step was to use other lanthanide salts (Table S1, entries 14–20) along with yttrium salts. Y<sup>III</sup> has a size and Lewis acidity similar to Ho<sup>III</sup>, and the use allows a catalytic reaction to be monitored with NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>15</sup>N, or <sup>89</sup>Y), because of its diamagnetic character. Astonishingly, Y(OTf)<sub>3</sub> showed similar excellent catalytic performance (Table S1, entry 14) to Dy(OTf)<sub>3</sub>,<sup>41</sup> and the lanthanide chlorides showed

poorest performance (Table S1, entries 15–20). The next task was to utilize a mixture of Ni and Ln salts (Table S1, entries 21–26), which showed that the presence of the Ni salt had an almost negligible influence on the catalytic performance. Finally, the use of Ni(ClO<sub>4</sub>)<sub>2</sub> and Dy(OTf)<sub>3</sub> or Y(OTf)<sub>3</sub> (Table S1, entries S27 and 28) showed an insignificant influence of the Ni source on the catalytic performance. The Y salt was better than the Dy salt. All these experiments demonstrated the superior catalytic behavior of **1Dy**<sup>47</sup> (use of only 1 mol %; see Table 1, entry 1) over the simple metal salts

Table 1. Comparison of 1Ln Source Catalytic Activity



| entry | catalyst   | temperature | loading <sup>b</sup><br>(mol %) | time (h) | yield <sup>c</sup> (%)     |
|-------|------------|-------------|---------------------------------|----------|----------------------------|
| 1     | <b>1Dy</b> | rt          | 1                               | 2        | quantitative <sup>47</sup> |
| 2     | <b>1Sm</b> | rt          | 1                               | 2 (24)   | 55 (75)                    |
| 3     | <b>1Eu</b> | rt          | 1                               | 2 (24)   | 60 (99)                    |
| 4     | <b>1Gd</b> | rt          | 1                               | 2 (24)   | 63 (99)                    |
| 5     | <b>1Tb</b> | rt          | 1                               | 2 (24)   | 63 (86)                    |
| 6     | <b>1Y</b>  | rt          | 1                               | 2        | quantitative               |
| 7     | <b>1Y</b>  | rt          | 0.5                             | 2 (24)   | 98 (100)                   |

<sup>a</sup>Reaction conditions: 1 mmol amine, 0.5 mmol 2-furaldehyde, 100 mg of 4 Å molecular sieve (MS), 4 mL of anhydrous MeCN catalyst, room temperature (rt). <sup>b</sup>Catalyst loading calculated per equivalent of Dy. <sup>c</sup>Determined by <sup>1</sup>H NMR spectroscopy.

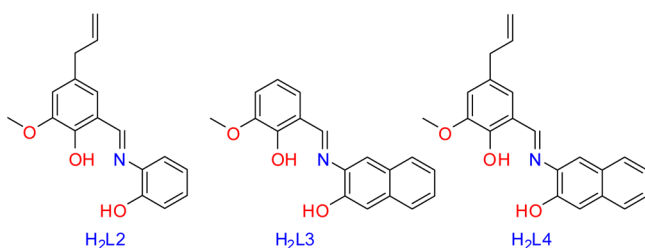
as catalysts and the insignificant role of Ni<sup>II</sup> in the catalysis. As shown in Table 1, **1Sm**, **1Eu**, **1Tb**, and **1Gd** (entries 2–5) catalyze the reaction in moderate to good yields in comparison to **1Dy** but show higher yields than simple salts. When **1Y** (Table 1, entry 6) was involved, a catalytic performance similar to **1Dy** was observed. A further decrease of the catalytic amount of **1Y** to 0.5% loading results in excellent conversion (Table 1, entry 7). The higher efficacy of Y<sup>III</sup> than Ln<sup>III</sup> in Lewis acid catalysis has been previously reported,<sup>70,71</sup> but no rationale has been proposed. All attempts to recover the 1Ln catalyst, in order to reuse it, were unsuccessful.

Taking into account the cost of the metal salts, the yttrium derivative (**1Y**) was used in further experiments.<sup>72</sup> Compound **1Y** shows similar or better catalytic behavior than **1Dy**, along with various secondary or primary amines (see Table 2).<sup>47</sup>

The excellent results that were obtained using even lower catalyst loadings (0.5% for **1Y**, instead of 1.0% for **1Dy**), along with the less-expensive lanthanide source, led us to consider the possibility that **1Y** could be structurally modified to achieve immobilization and demonstrate photosensitivity. We recently reported a library of 19 modified Schiff-base organic ligands that offer coordination environment similar to that in H<sub>2</sub>L1.<sup>68</sup> Among these, the three organic ligands shown in Scheme 2 were selected for the synthesis of the corresponding tetranuclear CCs. Other considerations were (i) to increase the solubility, as well to offer the possibility for deposition of these species on surfaces by the introduction of an allyl group (H<sub>2</sub>L2); (ii) to create “photosensitive” catalysts by inclusion of a naphtho group (H<sub>2</sub>L3); and (iii) to combine both of these features (H<sub>2</sub>L4).

Table 2. Comparison of Catalytic Activity of 1Y, 2Y, 3Y, and 4Y with Secondary and Primary Substrates, along with 1Dy,<sup>47</sup> for Comparison

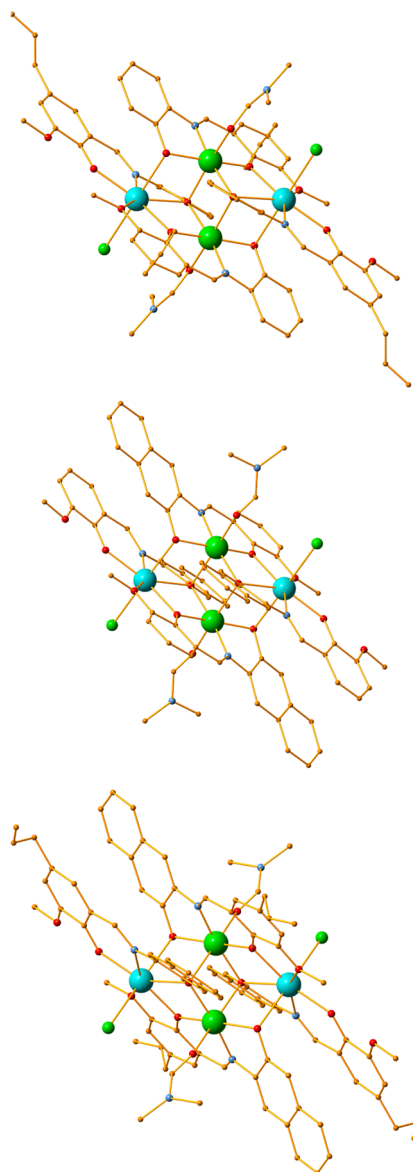
|       | Compound   | 1Dy          | 1Y           | 2Y       | 3Y           | 4Y       |
|-------|------------|--------------|--------------|----------|--------------|----------|
|       | Loading/ % | 1            | 0.5          | 1        | 0.5          | 1        |
|       | Time/h     | 16           | 8            | 12       | 8            | 12       |
| Entry | Product    | Yield/ %     | Yield/ %     | Yield/ % | Yield/ %     | Yield/ % |
| 1     |            | Quantitative | Quantitative | 91       | Quantitative | 85       |
| 2     |            | 99           | 96           | 85       | 95           | 80       |
| 3     |            | 95           | 99           | 70       | 94           | 64       |
| 4     |            | 61           | 53           | 58       | 51           | 52       |
| 5     |            | 63           | 71           | 69       | 69           | 62       |
| 6     |            | 96           | 99           | 96       | 99           | 94       |
| 7     |            | 62           | 91           | 91       | 93           | 91       |
| 8     |            | 70           | 95           | 94       | 94           | 92       |
| 9     |            | 26           | 90           | 81       | 86           | 81       |

<sup>a</sup>Reaction conditions: 1 mmol amine, 0.5 mmol 2-furaldehyde, 100 mg of 4 Å MS, 4 mL of anhydrous MeCN catalyst, and room temperature.<sup>b</sup>Catalyst loading calculated per equivalent of 1Ln. <sup>c</sup>As determined by <sup>1</sup>H NMR spectroscopy.Scheme 2. Three Modified Organic Ligands (H<sub>2</sub>L2, H<sub>2</sub>L3, and H<sub>2</sub>L4) Used for the Synthesis of 2Y, 3Y, and 4Y, Respectively

From ligand H<sub>2</sub>L2 (Scheme 2, left), in a slightly different synthetic ratio to 1Y, a compound formulated as [Ni<sup>II</sup><sub>2</sub>Y<sup>III</sup><sub>2</sub>(L2)<sub>4</sub>Cl<sub>2</sub>(DMF)<sub>2</sub>] (2Y) (Figure 1A) was obtained. Also, the ligands H<sub>2</sub>L3 and H<sub>2</sub>L4 (Scheme 2, center and right),

with slightly different synthetic ratios, gave [Ni<sup>II</sup><sub>2</sub>Y<sup>III</sup><sub>2</sub>(L3)<sub>4</sub>Cl<sub>2</sub>(DMF)<sub>2</sub>] 2DMF 2Et<sub>2</sub>O (3Y 2DMF 2Et<sub>2</sub>O) (Figure 1B) and [Ni<sup>II</sup><sub>2</sub>Y<sup>III</sup><sub>2</sub>(L4)<sub>4</sub>Cl<sub>2</sub>(DMF)<sub>2</sub>] (4Y) (Figure 1C), respectively. These compounds were characterized by X-ray crystallography (Figure 1), IR, ESI-MS, and TGA (see the ESI). Single-crystal studies indicate that compounds 2Y, 3Y, and 4Y are isoskeletal<sup>68</sup> to 1Dy, while the ESI-MS data indicate that all three compounds retain their core structures in solution, shown by two main peaks corresponding to the {[Ni<sup>II</sup><sub>2</sub>Y<sup>III</sup><sub>2</sub>(L)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> and {[Ni<sup>II</sup><sub>2</sub>Y<sup>III</sup><sub>2</sub>(L)<sub>4</sub>]<sup>2+</sup> fragments. Each Ni<sup>II</sup> center coordinates to six atoms (O<sub>5</sub>N environment) possessing an octahedral geometry and each Y<sup>III</sup> center coordinates to seven atoms (O<sub>5</sub>NCl environment) possessing a pentagonal bipyramidal geometry.

The catalytic activity of 2Y, 3Y, and 4Y toward the prototype reaction is shown in Table 2. Compounds 2Y and 4Y are not as efficient, relative to 1Y (1.0% loading, instead of 0.5% loading,

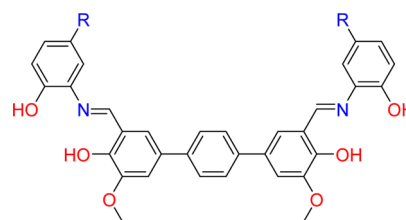


**Figure 1.** X-ray crystal structures of **2Y** (top), **3Y** (middle), and **4Y** (bottom). Color code: green =  $\text{Ni}^{\text{II}}$ ; light blue =  $\text{Y}^{\text{III}}$ ; yellow = C; red = O; pale blue = N; light green = Cl. Hydrogen atoms and disordered solvent molecules are omitted for the sake of clarity.

and slightly lower yields), but these results can be attributed to the presence of the sterically demanding naphtho groups. When **3Y** was employed as a catalyst (Table 2), yields similar to those with **1Y** were obtained. As we reported previously,<sup>47</sup> when the reaction occurs with primary amines, the corresponding deprotonated Stenhouse salts are formed (entries 6–9). The ring closing of the salt is promoted by the use of very dilute HCl, leading to the corresponding *trans*-4,5-diaminocyclopent-2-enones.

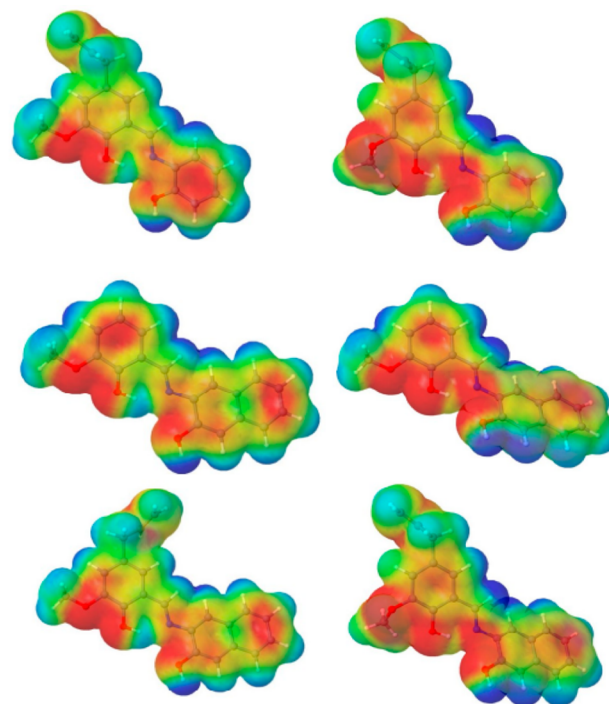
To explore further the possible immobilization of these catalysts, we attempted to synthesize the novel organic ligands **H<sub>4</sub>L5** and **H<sub>4</sub>L6** shown in Scheme 3 (see the ESI for synthesis details). Ligand **H<sub>4</sub>L5** offers a coordination environment similar to that in **H<sub>2</sub>L1**; therefore, it was expected to form coordination polymers upon complexation with the  $\text{Ni}^{\text{II}}$  and  $\text{Y}^{\text{III}}$  salts. However, **H<sub>4</sub>L5** is only slightly soluble in polar solvents such as *N,N'*-DMF or DMSO. Organic ligand **H<sub>4</sub>L6** was synthesized, expecting a higher solubility, but similar to **H<sub>4</sub>L5**, it is only

**Scheme 3.** Protonated Form of the Modified Organic Ligands **H<sub>4</sub>L5** ( $\text{R} = \text{H}$ ) and **H<sub>4</sub>L6** [ $\text{R} = \text{C}(\text{CH}_3)_3$ ]



slightly soluble in polar solvents. Our efforts to synthesize the corresponding coordination polymers have not yet been successful.

Computational studies showed that it was possible to modify ligand sterics without compromising the electrostatic properties that are key to the activities of the complexes. Renditions of the molecular electrostatic potential (MEP) for **H<sub>2</sub>L2**, **H<sub>2</sub>L3**, and **H<sub>2</sub>L4** are shown in Figure 2. The results also suggest that the charge distribution within the O–O–N–O core pattern directly interacting with the metals is a function of the conformation of the ligands.



**Figure 2.** Rendition of the molecular electrostatic potential (MEP) of **H<sub>2</sub>L2** (upper), **H<sub>2</sub>L3** (middle), and **H<sub>2</sub>L4** (lower) organic ligands: (left) bound and (right) free conformation.

## CONCLUSIONS

The collective data on this simple and high yielding isoskeletal series of  $\text{Ni}^{\text{II}}\text{Ln}^{\text{III}}_2$  CCs, supported by structurally homologous Schiff base ligands, shows remarkable catalytic activity in the formation of *trans*-4,5-diaminocyclopent-2-enones from 2-furaldehyde and primary or secondary amines. The  $\text{Ni}^{\text{II}}$  contribution is negligible and, therefore, it is safe to deduce that the domino reaction is driven solely by the 4f or Y ion. Remarkably, the employment of  $\text{Y}^{\text{III}}$  instead of  $\text{Dy}^{\text{III}}$  makes lower loading and lower-cost catalysts possible. We show that



the functionalization of the organic skeleton is feasible (**2Y**, **3Y**, and **4Y**), without impairing the catalytic activity. Moreover, our results suggest that the modified species **2Y** and **4Y**, which have allyl groups, can be immobilized by deposition on surfaces. Further work on this aspect is in progress. We are currently exploring the possibilities of utilizing 3d/4f or 3d/Y CCs as tandem catalysts in other organic transformations.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b00720.

ESI-MS, TGA, and IR of **1Ln**. ESI-MS, TGA and IR of **2Y–4Y**;  $^1\text{H}$  NMR, and ESI-MS of  $\text{H}_2\text{L1}$ ,  $\text{H}_2\text{L2}$ ,  $\text{H}_2\text{L3}$ ,  $\text{H}_2\text{L4}$ , and  $\text{H}_4\text{L5}$ ;  $^1\text{H}$  NMR of catalytic products from Table 2; Tables S1 and S2, Schemes S1 and S2, and Figures S1–S22 (PDF)  
Crystallographic data (CIF)

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### Notes

The authors declare no competing financial interest.

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